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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

A full series of alkyl and aryl sulfonated aramid and imidazole polymers with a range of ion contents have been synthesized and studied. Ion transport and ion binding in a polypyrrole-poly(pyrrolepropane sulfonate) copolymer has been examined. Studies of the high catalytic activity of polypyrrole-platinum nanocomposites have continued. Studies of band structure and low band-gap polyheterocycles using our recently developed Modified Extended Hückel method have also continued, as has the synthesis of new polythiophene derivatives containing ester side chains.

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Technical Report 37

**Electronic and Ionic Transport in Processable Conducting Polymers**

by

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## Description of Progress

A full series of alkyl- and aryl sulfonated aramid and imidazole polymers have been synthesized with a range of ion contents. At high ion contents both of the polymers form water soluble derivatives. The ternary phase behavior of these new polyelectrolytes with the rigid-rod polymer PBT and methanesulfonic acid has been investigated in detail. Both polyelectrolytes exhibit phase behavior that significantly varies from that expected for random coils mixed athermally with rigid-rods. The results suggest a "repeat-unit" interaction and serve to increase windows of miscibility from which rigid-rod polymers can be processed. With lower ion contents these ion-containing aramid and imidazole polymers behave as ionomers. Thermal and mechanical analyses are presently under way.

Studies have continued in the area of ion transport and ion binding in polypyrrole materials. A polypyrrole-poly(pyrrolepropanesulfonate) copolymer which is capable of binding multiply-charged cations and which is also permselective to cations such as  $K^+$  has been developed. A polypyrrole-platinum nanocomposite has been developed and studied which has high catalytic efficiency towards oxidation of  $H_2$  and reduction of  $O_2$ . The efficiency is close to that of bulk platinum with only about 4% of the quantity of platinum within the polymer matrix. The nature of the ionic transport in polypyrrole-poly(pyrrolepropanesulfonate) copolymer has been elucidated using quartz crystal microgravimetry.

We have used our recently developed Modified Extended Hückel band calculations along with conformational analysis on oligomers at the PRDDO level to study and develop new low band-gap polymers. A very promising system, currently being synthesized, is poly(thieno[3,4-b]thiophene), which is predicted to have a band gap comparable to that of polyacetylene.

Poly(3-decyloxycarbonylthiophene), a soluble polythiophene with a strongly electron withdrawing group on the thiophene ring, has been prepared by ferric chloride polymerization of the monomer and is being characterized and studied.

## **Publications**

### ***Papers Published***

Stickle, W. F.; Reynolds, J. R.; Jolly, C. A. "Surface Characterization of Electrically Conducting Nickel Tetrathiooxalate/Poly(vinyl alcohol) Composites", *Langmuir* **1991**, 7, 2460.

Panchalingam, V.; Reynolds, J. R. "Poly(1,3-cyclohexadiene-*alt*- $\alpha$ -fluoroacrylonitrile): A Thermally Stable, Alternating Copolymer", *J. Polym. Sci., Part A, Polym. Chem.* **1992**, 30, 967.

Ruiz, J. P.; Dharia, J. R.; Reynolds, J. R.; Buckley, L. J. "Symmetry Effects on the Physical and Electronic Properties of Processable, Electrically Conducting, Substituted Poly(di-2-thienylphenylenes)", *Macromolecules* **1992**, 25, 849.

Child, A. D.; Reynolds, J. R. "Separation of Neutral-to-Polaron and Polaron-to-Bipolaron Redox Events in Alkoxy Substituted Di-2-thienylphenylene Polymers", *J. Chem. Soc., Chem. Commun.* **1991**, 1779.

Rajeshwar, K.; Lezna, R. O.; de Tacconi, N. R. "Light in an Electrochemical Tunnel", *Anal. Chem.* **1992**, 64, 429A (cover story and article).

Basak, S.; Zacharias, P. S.; Rajeshwar, K. "Binding and Surface Coordination Chemistry of Copper(II) Macrocycles at Nafion-Modified Glassy Carbon Electrodes", *J. Electroanal. Chem.* **1991**, 319, 111.

Son, Y.; Rajeshwar, K. "Potential Modulated Ultraviolet-Visible and Raman Spectra of Polypyrrole Thin Films in Aqueous Electrolytes", *J. Chem. Soc., Faraday Trans.* **1992**, 88, 605.

Hong, S. Y.; Marynick, D. S. "Modified Extended Hückel Band Calculations on Conjugated Polymers", *J. Chem. Phys.* **1992**, 96, 5497.

### ***Papers in Press***

Qiu, Y.-J.; Reynolds, J. R. "Electrochemically Initiated Chain Polymerization in Pyrrole in Aqueous Media", *J. Polym. Sci., Part A, Polym. Chem.*, in press.

Bose, C. S. C.; Rajeshwar, K. "Efficient Electrocatalyst Assemblies for Proton and Oxygen Reduction: The Electrosynthesis and Characterization of Polypyrrole Films Containing Nanodispersed Platinum Particles", *J. Electroanal. Chem.*, in press.

Hong, S. Y.; Marynick, D. S. "A Theoretical Study of the Conformation and Electronic Structure of Phenylene-Pyrrole and Phenylene-Furan Copolymers", *Macromolecules*, in press.

### ***Papers Submitted for Publication***

Gieselmann, M. B.; Reynolds, J. R. "Water Soluble Polybenzimidazole Based Polyelectrolytes", *Macromolecules*, submitted for publication.

Bose, C. S. C.; Basak, S.; Rajeshwar, K. "The Electrochemistry of Polypyrrole Chloride Films", *J. Phys. Chem.*, submitted for publication.

Basak, S.; Bose, C. S. C.; Rajeshwar, K. "Electrochemical Quartz Crystal Microgravimetry of Poly{Pyrrole-co-[3-(pyrrol-1-yl)propane sulfonate]}", *Anal. Chem.*, submitted for publication.

### ***Talks/Papers Presented***

Reynolds, J. R.; Marynick, D. S. "To Polymerize or Not to Polymerize: That is the Question...Spin Density Effects on the Oxidative Polymerization of Heterocycles to Form Electrically Conductive Polymers", presented at the 203rd National Meeting of the American Chemical Society, San Francisco, California, April 1992. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1992**, 33(1), 1158.

Reynolds, J. R.; Victor, M.; Saffariannour, M. "Poly( $\alpha$ -fluoroacrylonitrile) and Poly( $\alpha$ -fluoroacrylonitrile-co-ethylvinylether) Copolymers: Potential 1:1 Alternating Copolymers with Applications as Dielectric Materials", presented at 203rd National Meeting of the American

Chemical Society, San Francisco, California, April 1992. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1992**, 33(1), 1162.

Reynolds, J. R.; Gieselman, M. B. "Aramid and Imidazole Based Polyelectrolytes", presented at 203rd National Meeting of the American Chemical Society, San Francisco, California, April 1992. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1992**, 33(1), 1056.

Reynolds, J. R.; Gieselman, M. B. "Aramid and Imidazole Based Polyelectrolytes: Physical Properties", presented at 203rd National Meeting of the American Chemical Society, San Francisco, California, April 1992. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1992**, 33(1), 931.

Hong, S-Y.; Marynick, D. S. "Understanding the Conformational Stability and Electronic Structures of Modified Polymers Based on Polythiophene", presented at 203rd National Meeting of the American Chemical Society, San Francisco, California, April 1992.

Rajeshwar, K.; Bose, C. S. C.; Basak, S. "Electrochemical Quartz Crystal Microgravimetry of Polypyrrole Thin Films", presented at PITTCON '92, New Orleans, Louisiana, March 1992.

Hong, S-Y.; Marynick, D. S. "Modified Extended Hückel Calculations on Conjugated Polymers", presented at Southwest Theoretical Chemistry Conference, Dallas, Texas, November 1991.

The following seminars describing DARPA/ONR funded research were presented:

Pomerantz, M. "Conducting Polyheterocycles", University of North Texas, November 1991.

Pomerantz, M. "Electrically Conducting Polymers", Oklahoma Baptist University, November 1991.

Rajeshwar, K. Seminar at the Society of Western Analytical Professors' Meeting, Las Vegas, Nevada, February 1992.

Rajeshwar, K. "Quartz Crystal Microgravimetry: New Electroanalytical Application Possibilities for an Old Technique", University of New Mexico, April 1992.

Rajeshwar, K. "Quartz Crystal Microgravimetry: New Electroanalytical Application Possibilities for an Old Technique", University of Houston, May 1992.

### **Visitors to UTA**

Professor M. Cocivera from the University of Guelph visited on October 2, 1991, and presented a seminar entitled "Electrochemical Growth and Characterization of Group II-VI Semiconductors".

Professor J. M. Tour from the University of South Carolina visited on October 4, 1991, and presented a seminar entitled "Conjugated Oligomers and Polymers for Electronic and Photonic Applications".

Dr. Gregory Nelson from Hoechst-Celanese Corp. visited on January 31, 1992, and presented a seminar entitled "The Role of Polymer Modeling in Modern Chemical Industry".

Dr. Kang Lee from Monsanto Chemical Co. visited on February 21, 1992, and presented a seminar entitled "Synthesis and Characterization of Polymers for Electronic Applications".

Professor S.-M. Park from the University of New Mexico visited on March 27, 1992, and presented a seminar entitled "Electrochemical and Spectroscopic Studies of Several Conducting Polymers".

### **Personnel Changes**

Professor John R. Reynolds has moved to the Department of Chemistry at The University of Florida where he continues to actively participate in the DARPA/ONR funded URI program as a subcontractor.

Dr. S-Y. Hong, former postdoctoral associate, has left for a faculty position at Koshin College, Pusan, South Korea.

Dr. Yong Son, former postdoctoral associate, has left for a postdoctoral appointment with Professor S. Holdcroft at Simon Fraser University, British Columbia.

Melinda B. Gieselman, graduate student, has completed her doctoral requirements and is employed at 3M Co. in St. Paul, Minnesota.

Jose P. Ruiz received his doctoral degree and is employed at American Cyanamide in Stamford, Connecticut.

#### **Additional Noteworthy Items**

Krishnan Rajeshwar is organizing a Symposium on the Electrochemistry of Conducting Polymers for the Fall 1992 American Chemical Society Meeting in Washington, D. C.

Ronald Elsenbaumer has joined UTA as Chairman of the Materials Science and Engineering Department and Professor of Chemistry. He has been a world leader in the area of conducting polymers for the past 14 years at Allied-Signal Corporation.